

A Six-Crossing Doubly Interlocked [2]Catenane with Twisted Rings, and a Molecular Granny Knot

Jonathan J. Danon, David A. Leigh,* Simone Pisano, Alberto Valero, and Iñigo J. Vitorica-Yrezabal

Abstract: A molecular 6_3^2 link (a six crossing, doubly interlocked, [2]catenane with twisted rings) and a $3_1\#3_1$ granny knot (a composite knot made up of two trefoil tangles of the same handedness) were constructed by ring-closing olefin metathesis of an iron(II)-coordinated 2×2 interwoven grid. The connections were directed by pendant phenyl groups to be between proximal ligand ends on the same faces of the grid. The 6_3^2 link was separated from the topoisomeric granny knot by recycling size-exclusion chromatography. The identity of each topoisomer was determined by tandem mass spectrometry and the structure of the 6_3^2 link confirmed by X-ray crystallography, which revealed two 82-membered macrocycles, each in figure-of-eight conformations, linked through both pairs of loops.

Links (generally termed “catenanes” when referring to molecular systems) are mechanically connected closed loops (macrocycles).^[1] Complex links are found in some proteins^[2] and DNA.^[3] Topologies with two or three small-molecule components that have succumbed to synthesis include Hopf links^[4] (the simplest [2]catenane topology; a 2_1^2 link in Alexander–Briggs notation^[5]), Solomon links (4_1^2),^[6] a Star of David catenane (6_1^2),^[7] Borromean rings (6_3^3),^[8] and 6_3^3 ^[9] and 9_7^{10} links.^[11] The topologies with two components and fewer than seven crossings that have yet to be prepared in small-molecule form are the Whitehead link (5_1^2),^[12] and 6_2^2 and 6_3^2 links (types of two-component links with twists in the rings).^[13] Most of the complex molecular links synthesized to date are derived from metal coordination complexes that assemble ligand strands in spatial arrangements that direct the ring-closing reactions to generate the required topology.^[14] Types of motifs employed include orthogonally positioned ligand complexes,^[15] linear^[16] and circular^[17] metal helicates, and interwoven molecular grids.^[6m] A 2×2 interwoven grid was previously used to synthesize a Solomon

link by connecting the ends of parallel ligand strands.^[6m] However, the possibility of accessing different topologies from alternative ligand connectivities using similar types of scaffold remained unexplored. Herein we report on the designed synthesis of one of the topologies missing from the molecular lexicon, a 6_3^2 link, via a 2×2 interwoven grid. Also formed is a $3_1\#3_1$ ^[18] (granny) composite^[10,19] knot.

The 6_3^2 link^[13] consists of two constitutionally identical macrocycles involving six crossings, the same number as a Star of David catenane (6_1^2 link) but with a different crossing pattern. The topology can be depicted as two figure-of-eight shapes linked through both pairs of loops (Figure 1). The crossing pattern for this link can, in principle, be achieved from a 2×2 interwoven grid by connecting the ends of ligand strands on the same face of the grid that are coordinated to adjacent metal ions. However, if the grid is a near-perfect square then each strand end is equidistant to the two closest ligand-ends and a mixture of two topoisomers will be obtained. The relative orientation of the connections on the two faces of the grid plane dictates the topology formed: a 6_3^2 link (the joined ends on one face are roughly perpendicular to the joined ends on the other face) or a granny knot (the

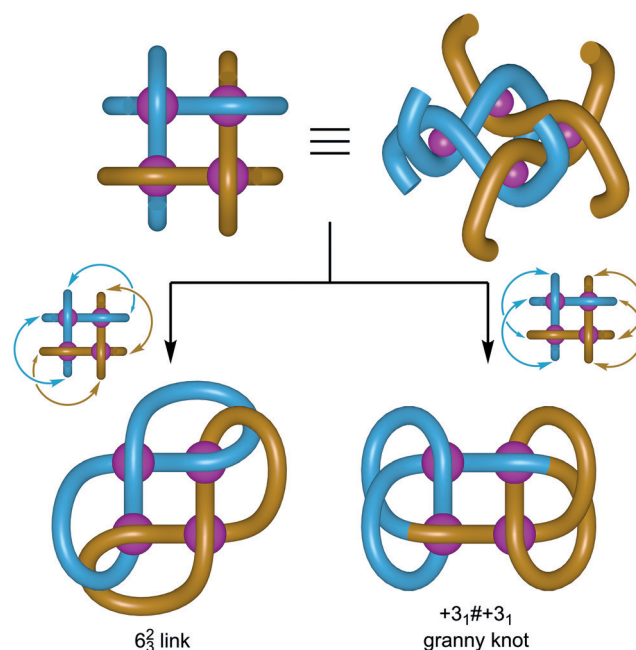


Figure 1. The topologies obtained by connecting the closest ligand ends on the same face of a 2×2 interwoven square grid. The knot and link topologies are both chiral,^[1,14,18] formed as a racemic mixture from a racemic grid.

[*] Dr. J. J. Danon, Prof. D. A. Leigh, S. Pisano, A. Valero, Dr. I. J. Vitorica-Yrezabal
School of Chemistry, University of Manchester
Oxford Road, Manchester M13 9PL (UK)
E-mail: david.leigh@manchester.ac.uk
Homepage: <http://www.catenane.net>

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connected groups on each face are close to parallel with those on the other) (Figure 1).

To achieve the required connectivity of the ligand strands, we designed bis-tridentate ligand **1** based on the bis(benzimidazolylpyridyl)thiazolo[5,4-d]thiazole scaffold previously used to assemble a Solomon link (Figure 2).^[6m] The *meta*-substituted phenyl groups (attached as part of a biphenyl unit) direct the pendant alkene chains above or below the grid plane, the biphenyl linkage significantly restricting the space accessible by the chain ends. The chain length was chosen to avoid over-reaching, permitting only the required strand connections. Ethyl groups were used to increase the solubility of the benzimidazole units. These are smaller than the isopentyl groups used in the Solomon link synthesis^[6m] to avoid sterically hindering the conformations of the alkene chains that lead to the required connections.

To confirm that the modifications of the ligand would not hamper grid formation, we prepared a model ligand with methyl groups in place of the alkene chains (Supporting Information, Section 2.5). Complexation of the ligand with an equimolar amount of iron(II) or zinc(II) tetrafluoroborate proceeded smoothly in a mixture of dichloromethane and acetonitrile at room temperature to quantitatively afford the corresponding 2×2 interwoven grids, which were characterised by NMR spectroscopy and X-ray crystallography (Supporting Information, Sections 2.5 and 3). The alkene-bearing 2×2 interwoven grid $[\text{Fe}_4\mathbf{1}_4](\text{BF}_4)_8$ was synthesized in analogous fashion, using ligand **1** and a small excess of iron(II) tetrafluoroborate (Supporting Information, Section 2.2). The ^1H NMR spectrum of $[\text{Fe}_4\mathbf{1}_4](\text{BF}_4)_8$ showed significant downfield shifts of the pyridine protons compared to the parent ligand (**1**), and a significant upfield shift of the benzimidazole proton H^s (Supporting Information, page 9 and Figure S55), which should face the pyridine ring of the perpendicular ligand strand in $[\text{Fe}_4\mathbf{1}_4](\text{BF}_4)_8$ and therefore is indicative of the anticipated grid structure.

The 2×2 interwoven grid $[\text{Fe}_4\mathbf{1}_4](\text{BF}_4)_8$ was subjected to ring-closing olefin metathesis (RCM) as a dilute solution (1 mM) in dichloromethane/nitromethane (3:1), employing the Hoveyda–Grubbs second generation catalyst^[20] under microwave heating in a sealed vial (Figure 2). After 3 h, ^1H NMR indicated complete consumption of the starting material, and electrospray ionization mass spectrometry (ESI-MS) showed multiply charged peaks corresponding to the successive loss of tetrafluoroborate counteranions from the fully-closed grid (Supporting Information, Figure S3). The crude product was demetallated (Figure 2) by treatment with a saturated aqueous solution of tetrasodium ethylenediaminetetraacetate (Na_4EDTA) to afford a mixture of the metal-free knot and link and other reaction byproducts, which were separated by preparative recycling size-exclusion chromatography (GPC) (Supporting Information, Sections 2.2 and 2.3).

The non-interlocked macrocycle and other, non-ring-closed, compounds obtained from the RCM reaction were removed from the knot and link in the first GPC cycles to give pristine **2/3** in 18% overall yield. However, the separation of the two topoisomers, which appeared as a single peak during the first few GPC cycles, proved to be far more challenging. After exhaustive recycling (15–17 cycles), two distinct peaks

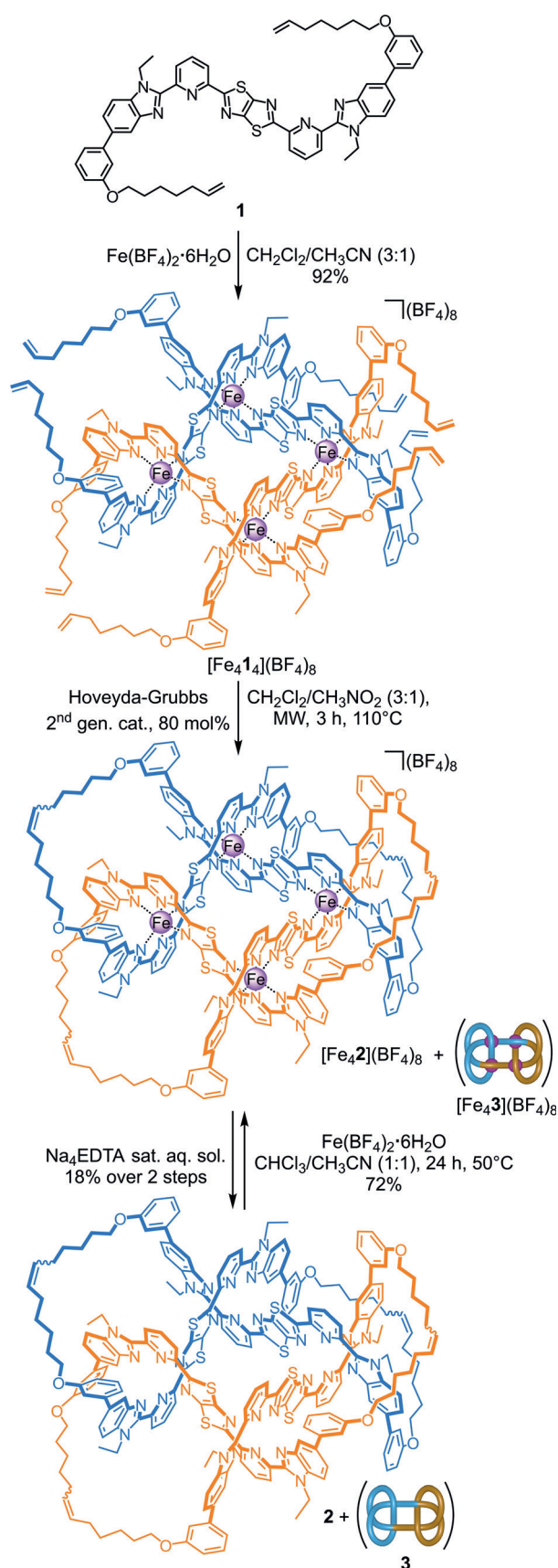


Figure 2. Metal-directed synthesis of 6^2_2 link **2** and granny knot **3** from ligand **1**.

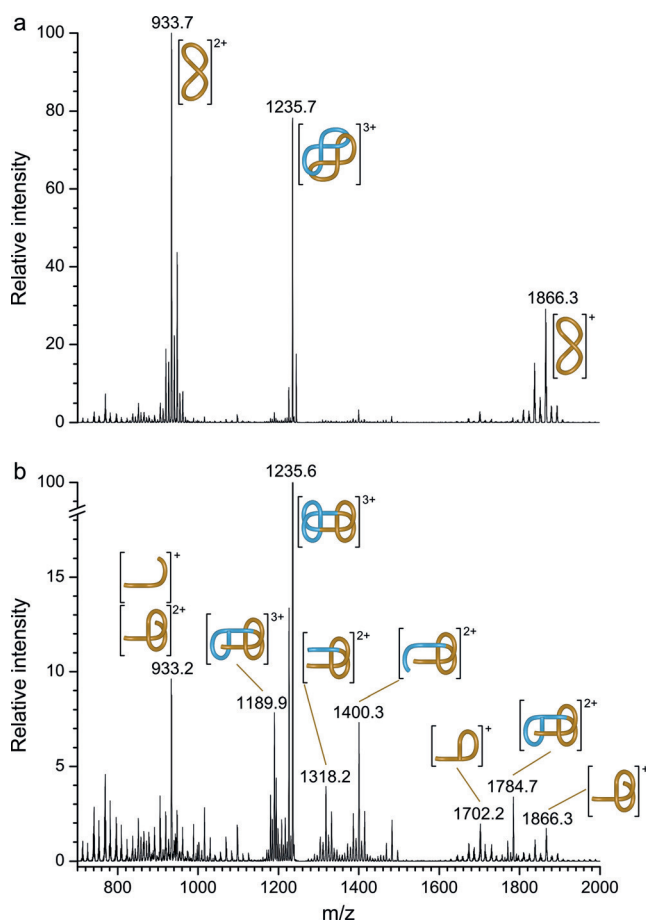


Figure 3. ESI-MS/MS tandem mass spectra of the $[M + 3H]^{3+}$ ion for a) 6_3^2 link **2** and b) granny knot **3**.

were obtained, the identities of which were determined by tandem ESI-MS. The faster eluting compound gave a series of tandem MS peaks (Figure 3b) that correspond to linear fragments that can only arise from the composite knot (fragmentation of the same bonds in a link would lead to dethreading and lower masses corresponding to the intact charged component macrocycle^[21]). Under the same conditions, the equivalent ion of the slower eluting fraction fragmented to singly and doubly charged macrocycle without any higher mass fragments, behaviour only consistent with a link topology (Figure 3a). Both topoisomers were also characterised by ^1H and ^{13}C NMR, giving distinct but complex spectra (Supporting Information, Section 2.3). The broad ^1H NMR spectra are typical of slow reptation of interwoven strands in large and complex molecular knots and links (Supporting Information, Figure S10).^[7,22,23]

The individual topoisomers were each remetalated by treatment with excess iron(II) tetrafluoroborate in a chloroform/acetonitrile mixture under heating (Figure 2 and Supporting Information, Section 2.4). In each case this proceeded with full conversion to the corresponding metallated complex, $[\text{Fe}_4\mathbf{2}](\text{BF}_4)_8$ or $[\text{Fe}_4\mathbf{3}](\text{BF}_4)_8$ respectively. The ^1H NMR spectrum of each complex was significantly sharper than that of the mixture originally obtained from the RCM reaction (Supporting Information, Figures S2 and S40).

We attempted to grow crystals from a sample of $[\text{Fe}_4\mathbf{2}/\mathbf{3}](\text{BF}_4)_8$ obtained by remetalation of a mixture of the organic topoisomers that had been separated from other species by GPC (Supporting Information, Section 2.2). However, slow diffusion of toluene into a solution of $[\text{Fe}_4\mathbf{2}/\mathbf{3}](\text{BF}_4)_8$ in acetone yielded single crystals of, to our surprise, the demetalated 6_3^2 link. The coordination of thiazolo[5,4-d]thiazole ligands to Fe^{II} is rather weak^[6m] and it appears that the poor solubility of metal-free **2** causes it to crystallize from solution as it reversibly forms at very low concentration. The X-ray crystal structure of **2** (Figure 4 and Supporting Infor-

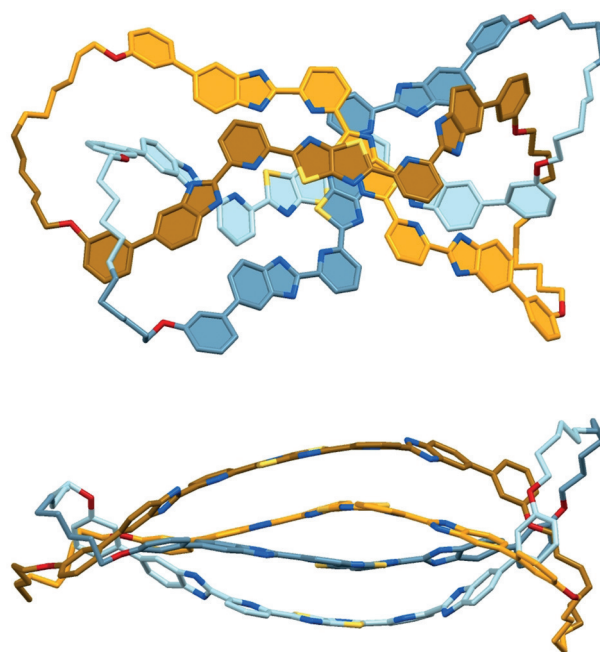


Figure 4. X-Ray crystal structure of the metal-free 6_3^2 link (**2**).^[25] Top view (top) and side view (bottom) showing the stacking of the ligand strands. Carbon atoms are coloured according to the macrocycle (the light blue and orange regions run below their darker blue and brown counterparts); N blue, O red, S yellow. A single enantiomer is shown; both enantiomers are present in the unit cell. The hydrogen atoms, pendant ethyl groups, and solvent molecules are omitted for clarity.

mation, Section 3) shows two 82-membered macrocycles, each with one twist, mechanically joined through both pairs of loops to form the six-crossing 6_3^2 link topology (Figure 4). A circa 3:1 *E/Z* mixture of alkenes is present in the alkyl chains. The aromatic regions of the ligand strands stack at the centre of the structure, with an average distance of about 3.5 Å between strands. From inspection of models it is clear that the 6_3^2 link is topologically chiral,^[1,18] both enantiomers are present in the unit cell.

The designed assembly of different molecular topologies is one of the last forms of isomerism still to be properly mastered through synthetic chemistry. Like natural product synthesis,^[24] the way the field is advanced is to demonstrate the synthesis of previously difficult to make or inaccessible structures. In doing so a toolbox of strategies, tactics, and methods is developed that can be used to tackle ever more

complex targets. The current work demonstrates that carefully designed ligand extensions can be used to direct the end-groups of interwoven strands on a 2×2 grid for connections that generate both a six-crossing two-component prime link and a granny composite knot.

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Conflict of interest

The authors declare no conflict of interest.

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- [18] In the composite knot nomenclature, $3_1\#3_1$ denotes that the two trefoil (3_1) tangles are of the same handedness, both + or both – (a granny knot), as opposed to $3_1\#3_1^*$ where the * would indicate two 3_1 tangles of opposing handedness (a square knot). See: S. D. P. Fielden, D. A. Leigh, S. L. Woltering, *Angew. Chem. Int. Ed.* **2017**, *56*, 11166–11194; *Angew. Chem.* **2017**, *129*, 11318–11347.
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